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PRELIMINARY ASSESSMENT OF ORGANOCHLORINE PESTICIDE RESIDUES IN THE SEDIMENT FROM SEVERAL ESTUARIES AND TAM GIANG - CAU HAI LAGOON, THUA THIEN HUE, 2005

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SUMMARY

Organochlorine pesticide residue were determined in sediments collected from three estuary zones fowarding Tam Giang - Cau Hai Lagoon, Thua Thien Hue, Vietnam during the dry season in 2005. A total of 10 sediment samples were collected at the river estuaries and along the lagoon. Base on Sediment Criteria of Environmental Protection Agency (US EPA, 1999) [1] and the Canadian Environmental Quality Guidelines (Canadian EQG, 2002) [3], the site specific Sediment Criterion for specific contaminant was derived to help determine what concentrations of chemicals are likely to be associated with adverse biological effects. The concentrations these contaminants were in the range of 0.2 - 8.2 μg/kg sediment for DDTs, 4.9 - 92.4 μg/kg sediment for HCHs, 1.5 - 110 μg/kg sediment for aldrin & dieldrin and 0.6 - 27.9 for endrin. Most of results were exceeded the Sediment Criteria for Human Health Bioaccumulation. Some of them even exceeded the Wildlife Bioaccumulation Criteria and exceeded the Canadian Environmental Quality Guidelines. The results obtained in this study show that there still exist a variety of organochlorine pesticide residues in the sediments from the estuaries and lagoon of Thua Thien Hue province.

I - INTRODUCTION

Organochlorine pesticides such as DDTs, HCHs, Aldrin, Dieldrin and Endrin were known to have bioaccumulative nature because of their lipopilicity and persistency. In years of 1980s decade, DDTs, HCHs,… were widely used in agriculture and in public medical service in Thua Thien Hue. In the region, the annual rainfall is high, averaging 1,800 - 2,000 mm, floods and soil erosion happen yearly. This makes sediment to be transported into the mouths of rivers such as O Lau, Huong, and Truoi River. The pesticides residues associated with sediment also have been carried to these estuaries and into Tam Giang – Cau Hai lagoon. Sediment provides habitat for benthic biota and can be ingested by them. These organisms are then eaten by fish and birds, which can result in higher concentrations in people through aquatic and terrestrial food chains [1].

Tam Giang - Cau Hai lagoon with the area 22,000 ha, locate about 70 km length along the seaside and receive water from O Lau, Huong and Truoi rivers At present, about 300,000 residents (about 30% population of the province) are living on aquaculture in the lagoon region (data from Thua Thien Hue Fishery Dept., 2003). The quality of lagoon environment, therefore, is being paid much attention to.

II - MATERIALS AND METHODS

Sediments were collected at the middle of the dry season (April-July 2005) on three zones:

- The O Lau estuary next to Tam Giang;

- The Huong estuary next to Tam Giang;

- The Truoi estuary next to Thuy Tu and Cau Hai.

1. Contaminant analysis

Sampling and sample pre-treatment

At each of 10 sites, several samples were collected and pooled in order to obtain a representative sample. The analysis method was according to US EPA-methods: 3540C, 3620 B, 3660, 3665A, 508 for soxhlet extraction, Florisil clean- up, sulphur clean-up, sulphuric acid clean-up and determination for organochlorine compounds, respectively [2].

Sediment samples were wet sieved through a metallic screen and the fraction with particle size < 0.1 mm was used. Samples were kept in a deep freezer at -20^{o}C until analysis.

2 g of sediment was taken and mixed with 2 g of anhydrous Na_2SO_4. Sample extraction was carried out by mixing with 100 ml *n*-hexane in soxhlet extractor for 12 hours. The extracts were concentrated on a rotary evaporator and then reduced the volume to approximately 2 - 5 ml.

The extracts were treated with activated Cu powder to remove sulfur compounds, then by florisil column and follow with H_2SO_4 before performing chromatography.

Contaminant quantification

Analyses of the samples were carried out using a programmed temperature gas chromatograph equipped with mass spectroscopy QP-2010-GC-MS with DB-1 column. Quantification of the contaminants is based on the internal standard method using pyren-d10. Final results are expressed in dry weigh basis.

2. Organic carbon analysis

It was carried out using Walkley-Black method [3]. The sample was reacted in $K_2Cr_2O_7$ 1 N and concentrated H_2SO_4 solution for a half of hour. The received solution was titrated using Mohr solution. The concentration of organic compounds in the sample was derived:

organic compounds (%) = 0.39K (V_0-V_1)N and organic carbon (%) = organic compounds (%): 2.

in which:

K: dry weigh concentration;

V_0: the volume of Mohr solution for the blank sample;

V_1: the volume of Mohr solution for the sediment sample;

N: the concentration of Mohr solution;

2: conversion factor.

3. Assessment method

a) The Sediment Quality Criteria

Concentrations of DDTs, HCHs, aldrin and dieldrin, endrin defined in sediments in some estuaries were compared with the Sediment Citeria of Environmental Protection Agency (US EPA, 1999) [4] and the Canadian Environmental Quality Guidelines (Canadian EQG, 2002) [5]. The Sediment Criteria have been established for certain contaminants to help determine what concentrations of chemicals are likely to be associated with adverse biological effects. Within the framework of New York State water quality regulations, five primary levels of protection are identified (6NYCRR, 1991). From which sediment criteria can be derived to different levels.

Sediment Quality Criteria for Non- Polar Organic Compounds using Equilibrium Partitioning (EP) methodology. The basic for EP methodology is that the toxicity of a contaminant in sediment is attributable to the concentration of the contaminant that dissolves in the interstitial pore water, and is considered to be freely biologically available [1].

When a non-polar organic contaminant enters the sediment, it will partition between the sediment and pore water in three compartments: a fraction will adsorb to the organic carbon in the sediment another fraction will adsorb to dissolved organic carbon in the interstitial pore water; and a third fraction will dissolve in the pore water. The equilibrium will be established so that any change in the contaminant concentration in one compartment will result in a corresponding change in the contaminant concentration in other compartments.

b) Accounting

The organic carbon normalized contaminant sediment criterion SC_{OC}

$$SC_{OC} = WQC \times K_{OW}$$

WQC: Water quality criterion for each contaminant (µg/l) in US Sediment Criteria

K_{OW}: the octanol/water partition coefficient, very similar with sediment organic carbon/water partition coefficient for a non-polar organic contaminant (l/kg)

SC_{OC}: the organic carbon normalized contaminant sediment criterion (µg/gOC; OC: organic carbon)

For example, the DDT Water quality criterion WQC for the level of protection of piscivorous wide life from bioaccumulation is 0.001 µg/l, the K_{OW} for DDTs is 10^6 l/kg. The organic carbon normalized DDTs sediment criterion SC_{OC} would be:

DDT SC_{OC} = 0.001 µg/l × 1,000,000 l/kg × 1kg/1,000 g OC = 1 µg/gOC

(1 kg/1,000 g OC is a conversion factor; OC: organic carbon)

The meaning of the criterion is that based on the equilibrium partitioning characteristic of DDTs, in order not to exceed the water quality criterion of 0.001 µg/l in the pore water, the concentration of DDTs in the sediment must not exceed 1 µg for each gram of organic carbon in the sediment.

The site specific sediment criterion (SC) for a contaminant

To apply this SC_{OC} on a site specific basis, the concentration of organic carbon in the sediment at the site must be know. For example, if the concentration of DDTs in 1-OL sediment sample was know to contain 1.62% organic carbon, the site specific sediment criterion (SC) for DDT could be derived:

$$SC = SC_{OC} \times f_{OC}$$

f_{OC} = 1.62%OC/kg sediment = 16.2 gOC/kg

DDT SC = 1 µg/gOC × 16.2 gOC/kg = 16.2 µg DDTs/ kg sediment

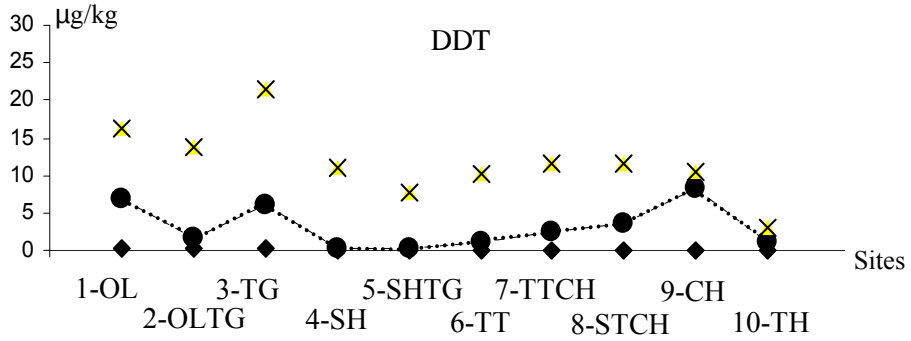
This criterion states that: if there are less than 16.2 µg DDTs/kg in sediment containing > 1.62% organic carbon, there is no appreciable risk to piscivorous widelife from consuming fish or other aquatic life from the water body over the contaminated sediment.

III - RESULTS AND DISCUSSION

Measured values of oganochlorines was compared with Sediment Criteia calculated for a specific site, the results was presented in Fig. 1– Fig. 4.

For DDTs (Fig. 1)

In mid-1980s, DDTs was heavily used to control malaria in Thua Thien Hue, especially in Nam Dong, A Luoi district, upstream of Truoi River. The high yearly rainfall and erosion can be the cause of transporting DDTs to the downstream of Truoi River and entering Cau Hai lagoon so that the concentration of this oganochlorine compound is very high here.



• Measured values ◆ Human Health Bioaccumulation ▲ Benthic Aquatic Life Chronic Toxicity × Widelife Bioaccumulation

Figure 1: Measured values of DDTs compared with Levels of US Sediment Criteria

Once enter to environment DDT can breaks down to DDE, DDD and some other species, which are also toxic and resistant. DDTs detected in all sediment samples were higher than the Levels of Human Health Bioaccumulation and Wide life Bio-accumulation. Total DDT in all samples exceeded the Sediment Quality Criteria for Level of Human Health Bioaccumulation about 10 - 80 times. The highest value of DDTs was 8.2 µg/kg at the 9-CH site; the lowest one was 0.2 µg/kg at 4-SH

Canadian Environmental Quality Guidelines (Canadian EQG, 2002) for DDE in sediment (probable effect level of 3.74 µg/kg marine sediment) was exceeded at three of 10 studied sites (1-OL, 3-TG, 9-CH). In general, comparing with US EPA 1999 or Canadian EQG 2002, the results show that the residue of DDT is the risk for environment.

- For HCHs (Fig. 2)

HCHs were very high in samples of 1-OL, 3-TG and 7-TTCH, they exceeded the levels, except the Level of Benthic Aquatic Life Acute Toxicity. This is suitable with the fact that HCHs is a popular pesticide and widely used in agriculture. Along O Lau River's banks with 10 km long from upstream to downstream, there is hundreds of hectare of rice. The use of agrochemical, especially HCHs, makes this region be polluted. Although the downstream of this river was zoning to establish a Bird Conservation Area, there are some environment problems that have to be concerned.

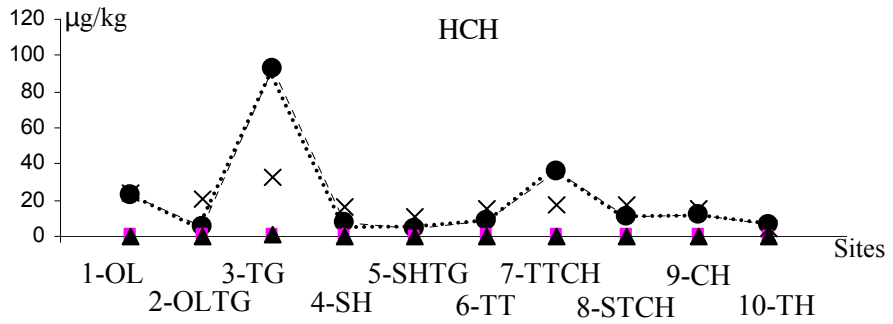
The probable effect level of Canadian EQG 2002 was only 0.99 µg/kg marine sediment. All the measured data of HCH were exceeded from 6 to 90 times (5.56 µg/kg at 2-OLTG to 92.38 µg/kg at 3-TG site).

- For Aldrin &dieldrin (Fig. 3)

Six samples (from 1-OL to 6-TT) in O Lau – Tam Giang, Huong – Thuy Tu areas, which have low concentration of these oganochlorine contaminants, but 4 remain samples (from 7-TTCH to 10-TH) in Truoi – Cau Hai area that have very high concentration of these two contaminants. The sample of 8-STCH contained the highest of aldrin and dieldrin with 110 µg/kg sediment. This is an unusual phenomenon. Although aldrin is used as a termiticide in urban areas but most of Vietnamese doesn't have the habit of using this chemical to protect their wooden appliances. The analysis results of four latter stations pose a big question, where is the source of these contaminants and why their concentration can high like that. The upstream of Truoi River belongs to Nam Dong and A Luoi district, which may be one of the sources of wood supplier for Thua Thien Hue province. To protect wood from the damage of termite a large amount of termiticide must have been used.

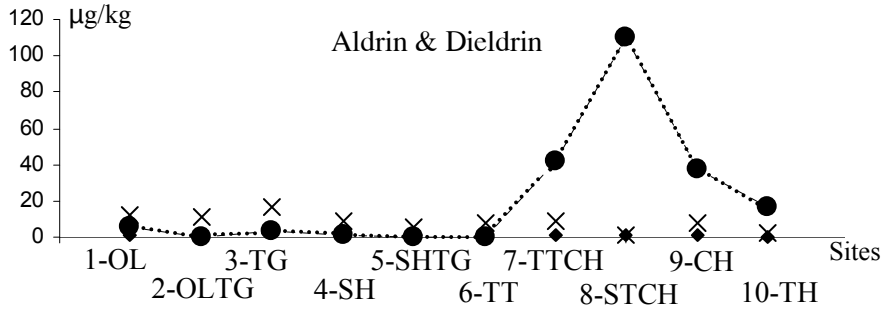
The measured data of these chemicals exceeded from 34 times higher (at 7-TTCH) to 91 times higher (at 8-STCH) compare with Human Health Bioaccumulation Criteria Level.

Comparing with probable effect level of Canadian EQG 2002 was only 0.99 µg/kg marine sediment, all the values of these four station exceeded from 17 times (at 10-TH) to 111 times (at 8-STCH).



• Measured values ◆ Human Health Bioaccumulation ▲ Benthic Aquatic Life Chronic Toxicity × Widelife Bioaccumulation

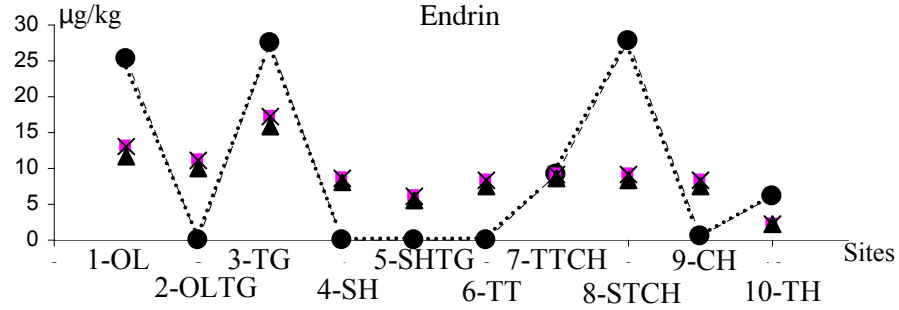
Figure 2: Measured values of HCHs compared with Levels of US Sediment Criteria



• Measured values ◆ Human Health Bioaccumulation ▲ Benthic Aquatic Life Chronic Toxicity × Widelife Bioaccumulation

Figure 3: Measured values of aldrin and dieldrin compared with Levels of US Sediment Criteria

- For Endrin (Fig. 4)



• Measured values ◆Human Health Bioaccumulation ▲ Benthic Aquatic Life Chronic Toxicity × Widelife Bioaccumulation

Figure 4: Measured values of endrin compared with Levels of US Sediment Criteria

All the data of endrin concentration of 10 sites were presented in Fig. 4. In comparing with Human Health Bioaccumulation and Wildlife Bioaccumulation Levels, there are four of ten results exceeded the criteria. The highest exceeded level is two times higher than the criteria. There are four samples in which we can not detect endrin. The data of endrin show that this kind of chemical does not pose a potential risk for the environment.

IV - CONCLUSIONS

1. Most of organo-chlorine pesticide concentrations in the sediment from the estuaries in Thua Thien Hue were exceeded the Sediment Criteria for Human Health Bioaccumulation Level from US EPA 1999 criteria and Canadian EQG 2002 criteria. Some of them even exceeded the Wildlife Bioaccumulation Criteria. There are some environment problems that have to be concerned.

2. Contaminant concentrations were detected low in the sediment from Huong estuary, but the measured data detected were the very high at O Lau estuary and Cau Hai estuary. It is necessary to study in detail in these areas.

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